THE ASSOCIATION OF TRIMETHYLACETIC ACID IN CARBON TETRACHLORIDE

by

TEH-CHING CHIANG

B. S., Taiwan Normal University, Taipei, Formosa, 1960

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

Approved by:

Robert M. Hammaker
Major Professor

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Between the extremes of chemical bonds and van der Waals interactions there are interactions of intermediate energies which produce clusters of molecular aggregates called "complexes". The process of forming the complexes is called "association".

Hydrogen bonding is such an "associative interaction". The energy of breaking a hydrogen bond is of the order of a few kilocalories in contrast to the usual chemical bonds with energies of the order of tens of kilocalories and to the van der Waals interactions with energies of tenths of a kilocalorie.

"A hydrogen bond, A-H....B, is said to exist between a functional group A-H and an atom or a group of atoms B in the same or a different molecule when: a) there is evidence of bond formation and, b) there is evidence that the new bond linking A-H and B specifically involves the hydrogen atom already bonded to A," (24). The A-H group serves as a proton donor (an acidic group) and the B group serves as an electron donor (a basic group). Some examples of hydrogen bonds are: OH...O, OH...N, NH...O, NH...N, NH...F, and FH...F. Most commonly the proton is donated by a carboxyl, hydroxyl, amine or amide group. Also the proton bonded to a halogen or to a carbon can be active in association. The usual electron-contributing parts of the molecule are oxygen in carbonyls, ethers, and hydroxyls; nitrogen in amines and in N-heterocyclic compounds; and halogen atoms in particular molecular environments. If A-H and B are groups within a single molecule, the hydrogen bond formed is intramolecular and its formation causes chelation. On the other hand, if A-H and B are in different molecules, the hydrogen bond formed is intermolecular and its

formation causes molecular association.

Molecular association due to hydrogen bond formation is treated by the same methods as the formation of ordinary molecules, and the idea of a chemical equilibrium between the monomolecules and the associated complexes can be introduced (32). The most striking property distinguishing most associated complexes from most molecules is the rapid reversibility of the association under normal laboratory conditions (25).

Hydrogen bonding has been of great interest to chemists over the last three decades. The formation of a hydrogen bond in a solution or compound can modify a great many physical and a few chemical properties. Therefore, an investigator of hydrogen bonding is confronted by a variety of either spectroscopic or non-spectroscopic techniques. However, hydrogen bonding is still an incompletely understood phenomenon today.

One type of compound that forms intermolecular hydrogen bonds is carboxylic acids. In this research, the hydrogen bonding phenomenon of trimethylacetic acid will be investigated in carbon tetrachloride solution by spectroscopic techniques. The great value of solution for spectroscopic studies of hydrogen bonding lies in the possibility of controlling and determining the species present. At extreme dilution, intermolecular associations are eliminated or restricted to solvent-solute association only. At higher concentrations, intermolecular interactions become important but remain under control through the variables of temperature and concentration.

Of the various experimental techniques which may be used to study intermolecular hydrogen bonding, infrared spectroscopy has been a most fruitful technique due to the sensitivity of the vibrational spectrum

of a molecule to hydrogen bond formation. In addition, some advantages of infrared methods are that the species present in the system may be individually distinguished, low concentrations can be used and wide temperature ranges are accessible.

Proton magnetic reasonance (PMR) studies of hydrogen bonding have attracted great interest in the past decade due to the sensitivity of the electronic environment of the hydrogen atoms to hydrogen bond formation. The studies of hydrogen-bonded complexes can be made by PMR techniques even in the rather high concentration range which may be necessary in some cases. PMR also has been a useful tool in measuring changes in the amount of hydrogen bonding in fluid systems. However, the short life time of a proton in a given environment compared to the inverse of the chemical shift difference between various environments results in an averaging of the proton-shielding parameters and only one signal is observed (1). The position of this signal corresponds to the average environment of the various equilibrium processes involved in the hydrogen bonding. This is a particular disadvantage in a system in which polymeric association via hydrogen bonds occurs, because the variation of averaged nuclear-shielding parameter with concentration or temperature does not provide enough information for the obtaining of a true association chemical shift (5). In order to avoid this difficulty, trimethylacetic acid was chosen for this research. Of course, both the IR and PMR techniques have their limitations. IR is more specific than PMR; however, the absorption overlap may cause uncertainty due to arbitrary correction for absorption overlap. Consequently, the measurements may be limited to certain concentration ranges only. Actually there is no single type of technique

that is significantly superior to the other types with respect to both accuracy of measurement and specificity of the hydrogen bonding situation observed. In this research, IR and PMR techniques will be used supplementarily.

Johnson and Nash (19) have studied the association of trimethylacetic acid in the vapor phase by precise determination of vapor densities over the temperature range 80 to 200°C. The equilibrium constants log K_{12} $(mm_{Hg})^{-1} = -9.978 + 3063/T$, log K_{13} $(mm_{Hg})^{-2} = -18.29 + 5070/T$ and enthalpies $\Delta H_2 = -14.030$ kcal/mole, $\Delta H_3 = -23.200$ kcal/mole have been reported by them for the monomer $\rightleftharpoons$ dimer, and monomer $\rightleftharpoons$ trimer equilibria, respectively. Pohl et al. (23, 31) have studied the association of trimethylacetic acid in benzene by means of measurements of the electric polarization in very dilute solutions. The association constant $K_{12} = 6900\ M^{-1}$ is reported for monomer $\rightleftharpoons$ dimer equilibrium at 30°C. Reeves (34) has measured the hydroxyl proton chemical shift of trimethylacetic acid in carbon tetrachloride as a function of concentration at 28°C. Unfortunately, no more information has been reported. Chang and Morawetz (8) have measured the intensities of the carbonyl stretching mode of trimethylacetic acid in carbon tetrachloride solution near the 5.70 and 5.85 μ regions over a concentration range 3.16×10^{-3} - 32.4×10^{-3} M at 29.6°C. The monomer $\rightleftharpoons$ dimer equilibrium constant they reported is $K_{12} = 1730\ M^{-1}$ (at 29.6°C).

The general plan of this research is to take both the IR and PMR spectra of trimethylacetic acid in carbon tetrachloride solution over the accessible concentration range at several convenient temperatures. In the IR method both the spectra of the O-H stretching mode in the 3μ region

and C = O stretching mode in the 5.7μ region will be taken for the purpose of comparison. In the event that the optical densities and chemical shift measurements can be obtained satisfactorily, the further objectives to be attacked are:

1) To deduce the species present in the trimethylacetic acid - CCl_4 system and then to evaluate the equilibrium constants for hydrogen bonding at various temperatures.

2) To evaluate the monomer and dimer hydroxyl proton chemical shifts of trimethylacetic acid in CCl_4 solution at various temperatures.

3) To calculate the changes in standard enthalpy, ΔH^o, free energy, ΔG^o, and entropy, ΔS^o, for the hydrogen bond formation of trimethylacetic acid in CCl_4 solution by means of temperature variation studies.

EXPERIMENTAL

Materials

Carbon Tetrachloride. Fisher Scientific Co. spectro grade CCl_4 was dried by storing over P_2O_5 in a desiccator placed in a dry box for several days. After this treatment, spectrum of 1 cm of CCl_4 versus air showed no water absorption in the 2.7μ region.

Trimethylacetic Acid. Eastman "White label" trimethylacetic acid was purified by pumping with a mechanical vacuum pump on a sample of acid maintained close to its freezing point with a constant temperature bath. The operation, which was carried out in the apparatus shown in Fig. 1, was repeated until the acid freezing point was raised to 35.4°C. The drying apparatus was transferred to a dry box before being opened. The crystals were then stored over anhydrous P_2O_5 in a desiccator for

A. Sargent constant temperature relay unit.
B. Sargent constant temperature central heating and circulating unit.
C. Sargent constant temperature water bath.
D. Sample container.
E. Stopcock
F. Trap.
G. Cooling bath.

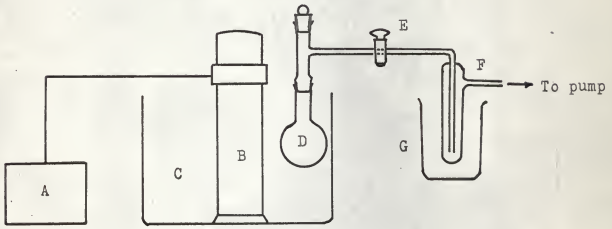


Fig. 1. Apparatus for purification of acid.

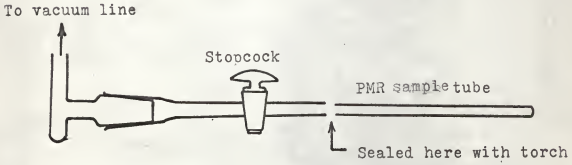


Fig. 2. Apparatus for filling and sealing sample tubes.

several hours before use.

Cyclohexane. Fisher Scientifc Co. spectro grade cyclohexane was distilled prior to use.

Carbon Disulfide. Fisher Scientific Co. spectro grade carbon disulfide was used without further treatment.

Dry Box

It was found that keeping the dried trimethylacetic acid, CCl_4 and solutions free from exposure to atmospheric moisture was very essential to the experimental results of this research. Therefore, a dry box was used.

The two-compartment dry box used was made of wood with glass windows and rubber gloves. The larger compartment (3'x3'x2') contained a balance and was used for preparing solutions and filling sample containers. The smaller compartment (1'x1'x1') was used as gas lock only. The inside of the box had been painted with synth-Epoxy paint (La Pine Scientific Co.) and the places where leakage might occur were all carefully sealed with Silastic RTV 732 silicone rubber. Doors were lined with silicone rubber coated sponge rubber weather strips (Johns-Manville, Chicago, Ill.) along their edges. With this treatment, the box was tight enough to maintain the rubber gloves parallel to the floor for about two hours after nitrogen gas had been admitted to the box. In order to obtain a low dew point inside the box, nitrogen gas was dried and recirculated in the following manner:

The recirculation system consisted of the following components supplied by Air Controls Inc. (Narbeth, Pa.): 08-000-77 Dia-Pump Recirculator--

Model EFB, 11-550-70 Main Desiccant Tube, and 11-551-70 Clear Indicating Dessicator. The two desiccant tubes (80 cm in legth with 4 cm innner diameter) were installed on the top of the larger compartment. The first tube, which was made of transparent acrylic plastic, was filled with indicating silica gel and the second tube constructed of anodized aluminum was filled with a more efficient desiccant, Linde type 13 x Molecular Sieve. Nipples at both ends of the aluminum tube were inserted into the box and the transparent tube was connected to the aluminum tube at one end by a short rubber hose. The other end of the aluminum tube was connected to a DIA-pump, a diaphragm-type compressor, and a nitrogen source was connected to the other end of the transparent tube. When the system was in opration, nitrogen gas from a cylinder (NCG water pumped) was passed through a 4 ft glass column packed with indicating silica gel and Linde 13 x Molecular Sieve and was drawn in from time to time through the transparent tube and further dried by the indicating silica gel. The pre-dried nitrogen gas was then passed into the aluminum tube to be further dehydrated before being channeled into the larger compartment. The nitrogen gas from the larger compartment and the small amount of nitrogen gas drawn in from the cylinder through the transparent tube from time to time as needed passed through the Molecular Sieve again before being returned to the larger compartment. The small amount of nitrogen gas drawn in from time to time while the system was in operation maintained a slight positive pressure inside the dry box to prevent contamination of the interior by atmosphere air. The smaller compartment, which served as the nitrogen gas lock, permitted the transfer of objects in and out without destroying the low dew point in the larger compartment.

The N_2 gas used to flush the larger compartment before starting the recirculation system and to flush the gas lock for transfer in and out was passed through the 4 ft glass column packed with indicating silica gel and Linde 13 x Molecular Sieve.

Solutions

In order to minimize absorption of atmospheric moisture, all solutions were made in the dry box under a low dew point nitrogen gas. For the infrared measurements, solutions were made up in volumetric flasks by dilution of pure or a more concentrated trimethylacetic acid solution with pure CCl_4. For proton magnetic resonance measurements, solutions were made by volumetric flasks and both acid and CCl_4 were weighed so that either molarity or mole fractions could be used as the concentration unit. Since the trimethylacetic acid and CCl_4 may vaporize from the solution, it was desirable to make all transfers as quickly and carefully as possible by using pipets or glass droppers. In order to prevent loss of trimethylacetic acid (22) and CCl_4, all spectra were taken as soon as possible after the solutions were made.

Infrared Measurements

Spectrometer. The spectra of the fundamental O-H stretching and C = O stretching modes of trimethylacetic acid were taken with a Perkin-Elmer Model 221G spectrometer. The instrument is an automatic recording, double-beam infrared spectrometer utilizing a servo-driven attenuator to produce a true radiation null at the detector. It includes programmed slit operation, programmed scan speed, automatic speed suppression,

automatic gain control, ordinate scale expansion and compression. Abscissa presentation is linear in wave number and ordinate presentation is linear in transmittance over a 20 cm scale.

Table 1 lists the instrument settings when spectra were taken.

Table 1. Perkin-Elmer 221G IR spectrometer settings.

Suppression	3.2
Expansion	1X
Attenuator speed	110
Resolution amplifier gain	5.3
Slit	Program
Filter	Auto
Slit program	9.27
Source intensity	0.32 amp
Energy	AGc off
Scan time	30

Cell and Cell Thermostat. A 2.5 cm cell (Connecticut Instrument Company Type H Long-Path Liquid Cell) with NaCl windows and a ground glass stopper was used for taking spectra in the O-H stretching region and a 5 mm rock salt cavity cell (CIC Type E, Standard Cavity Cell) was used in the C = O stretching region.

The cell thermostat used was made by the Barnes Engineering Co. It was comprised of a variable temperature chamber (Model 10k) and a power supply unit. Tap water was used as coolant to circulate through the chamber jacket and the chamber temperature was monitored by a

copper-constantan thermocouple. The temperature was read from a potentiometer.

KBr window assemblies were used as chamber thermopane windows. By using this chamber, the cell was completely submerged in a controlled temperature environment so that temperature accuracy was increased and cell windows were much safer due to the elimination of thermal gradient. Moisture condensation on the chamber windows was largely eliminated because each window assembly was made of two crystal windows which were cemented together but separated by a dry air space.

The thermostat had been calibrated and results are listed in Table 2. At a given tap water temperature and flow rate, a definite temperature was obtained within an accuracy of $\pm$ 1°C for a given dial setting.

Table 2. Variable temperature control chamber calibration.
coolant: tap water at 20°C
flow-rate: 600 ml/minute

	Dial setting (divisions)	Input voltage (volts)	Temperature (°C)	Time required to attain temperature stabilization (minutes)
	15	17.5	28.6	30
	30	34.0	43.2	30
Heating	45	51.0	59.0	30
cycle	60	67.5	76.0	30
	75	85.0	94.0	25
	90	102.0	113.0	20
Cooling	21	25	7.5	15
cycle	43.5	50	-1.23	15

Taking the Spectra. In order to minimize exposure of samples to the atmosphere, solutions were transferred to cells in the dry box. A small desiccator with anhydrous P_2O_5 was used to carry the samples from dry box to the IR instrument.

At lower temperature, there was only slight vaporization of CCl_4 from solutions, therefore, spectra at various temperatures were taken for a sample by changing the chamber temperatures and keeping the solution unchanged. However, at higher temperatures, where the vaporization of CCl_4 became appreciable and changed the concentration of solutions, a solution was used just for one measurement. Time required to stabilize a given temperature was shorter than the values listed in Table 2, if solution was changed and temperature setting was unchanged.

Proton Magnetic Resonance Measurements

Spectrometer. The PMR spectra of trimethylacetic acid were taken by using a Varian Model A-60 high-resolution analytical nuclear-magnetic resonance spectrometer. The instrument operates at 14,090 gauss field intensity and 60 Mc rotating field frequency. It includes automatic cycling of the magnet, NMR Field/Frequency control, self-stabilized operation and adjustable field sweep for base-line expansion of spectra.

Because the extreme requirement for homogenity of the magnetic field limited the volume of the sample to a few tenths of a milliliter, the solutions could only be measured at concentration as low as 0.14 molar concentration of hydrogen nuclei. Spectra were recorded by a graphic recorder on 25 by 50 cm calibrated charts. Chemical shifts were reported in cycles per second.

Thermostat. For the purpose of maintaining the samples at desired temperatures, a V-6057 variable temperature system was employed. The N_2 gas vaporizing from a 110 liter capacity tank of liquid nitrogen from Air Reduction Company Inc. was used as nitrogen gas supply. In the high-temperature range operations, 5 psi pressure and 14 cfh flow-rate were used, and the temperatures were calibrated by the chemical shifts of ethylene glycol. In the low-temperature range operation, 10 psi pressure and 14 cfh flow-rate were used, and the temperatures were calibrated by the chemical shifts of methanol. A mixture of dry ice and acetone in a Dewar was used in the cooling bath for the low temperature range operations. Stable temperature was obtained for a dial setting of V-6040 Temperature Controller with temperature regulation of $\pm$ 2°C at the samples.

Taking the Spectra. All solutions were transferred to PMR sample tubes in the dry box so that there was no moisture absorption during the transfers of solutions. In order to protect samples from vaporization or moisture absorption, sample tubes were sealed by oxygen torch instead of using tygon stoppers after the sample tubes had been filled. The apparatus used for filling and sealing the tubes is shown in Fig. 2. The apparatus was attached to a vacuum line and the sample frozen with liquid nitrogen. The stopcock was opened and the tube pumped out. The stopcock was closed and the apparatus removed from the vacuum line. The tube was then sealed off with a torch.

In order to avoid bulk magnetic susceptibility corrections, hydroxyl proton chemical shifts were measured by using the methyl peak of the trimethylacetic acid as the internal reference. In the concentration

range measured, hydroxyl proton chemical shifts are about 700 cps down field from the methyl peak. For the purpose of base-line expansion of spectra, the 500 cps sweep width was used instead of 1000 cps, therefore, sealed capillary tubes filled with benzene were used as external references to measure chemical shifts from benzene to hydroxyl proton peaks and also from methyl to benzene peaks. Thus, two 500 cps sweeps were made for each sample.

Spectra at a desired temperature were taken for all samples by changing the samples and keeping the temperature controller setting unchanged. A period of five minutes was required to attain temperature stabilization for each sample changed.

Near Infrared

It was expected that the first overtone spectra would provide a method of further separation of the non-hydrogen bonded O-H stretching frequency from that of the other species because the absorptions were spread out relative to the fundamental spectra by a factor of two, and for alcohols it has been found that the bonded O-H band is very weak relative to the free O-H band in the overtone region (the reverse is true in the fundamental region) (14). A study in the O-H stretching overtone region of trimethylacetic acid in CCl_4 solutions around 1.4 to 1.7 μ has been attempted. A Perkin-Elmer 4000 A spectracord, a double-beam instrument with tungsten lamp source, quartz prism monochromator and lead sulfide cell detector, was used. It was found that both the monomer band at 1.43 μ and the dimer band at 1.7 μ were overlapped badly so that it was not possible to make accurate measurements

of the optical densities.

Ultraviolet

It is expected that the UV spectrum of a molecule may be altered by the formation of a hydrogen bond if the chromophoric portion of the molecule is perturbed by the hydrogen bond. Therefore, UV spectra have received considerable attention as a means of studying hydrogen bonding in the past decade.

In this research, a UV study of trimethylacetic acid association in cyclohexane also has been attempted by using a Cary 11 spectrophotometer, a double-beam visible and ultraviolet instrument. Cyclohexane was used as solvent because it has no absorption in the UV region. There was no spectrum found from 400 mμ to 250 mμ for the acid, but a continuous absorption was observed starting at 250 mμ and extending to 210 mμ which was the shortest wave length the Cary 11 instrument could attain. When different concentrations were used, almost the same shape of absorptions appeared. It was not possible to measure the frequency shifts or vibrational fine structures to determine the concentrations of bonded and unbonded species (26).

Fundamental Region of O-H Bending

A study of the fundamental O-H bending of trimethylacetic acid in CS_2 solution around 7.0, 10.7 and 15μ (37) was attempted by using the Perkin-Elmer 337 infrared spectrophotometer. Bands obtained for different concentrations near 10.7μ clearly showed the dimer O-H bending characteristic absorption; however, the monomer bands near 15μ were less accurate for

measuring the optical densities because of the appreciable absorption of CS_2 in this region.

ANALYSIS OF SPECTRA AND EXPERIMENTAL DATA

Infrared

Beer's law for peak height intensities may be written in the form

$$\log \frac{I_o}{I} = \epsilon lc$$

where

I_o = energy of the incident radiation.

I = energy of the transmitted radiation.

ϵ = molar absorption coefficient at the given frequency.

l = cell length in cm.

c = molar concentration of the solution measured.

When the spectra are recorded as per cent transmission, the experimental quantities obtained are I_o and I.

O-H Stretching Mode. The typical spectra of O-H stretching of trimethylacetic acid in CCl_4 solution at various concentrations and temperatures are shown in Fig. 3. The 2.5 cm cell was used without matching at the reference beam because only one 2.5 cm cell was available.

The absorption band at 3530 cm^{-1} region is a sharp band with frequency independent of temperature and concentration within the accuracy of the measurement. The ratio of optical density to acid concentration increases with increasing temperature or decreasing concentration. Because as temperature increases or concentration

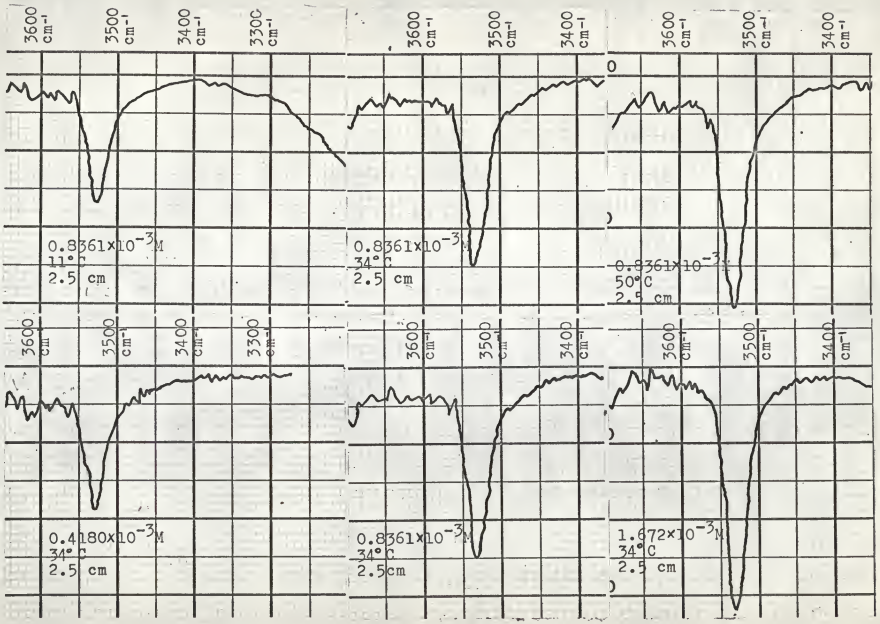


Fig. 3. Trimethylacetic acid in CCl_4 solution. O-H stretching mode.

decreases the amount of monomeric acid should be increased, the 3530 cm^{-1} band is thus assigned as the free O-H stretching band. The broad band around 2970 cm^{-1} shows optical density decreasing with increasing temperature or decreasing concentration. Because as temperature increases or concentration decreases the amount of polymeric acid should be decreased, the 2970 cm^{-1} band is thus assigned to the associated O-H stretching band.

The O-H stretching frequency shift from 3530 cm^{-1} to 2970 cm^{-1} accompanying the formation of a hydrogen bond may be explained as the change brought about in the potential function of the O-H stretching mode when it participates in a hydrogen bond (27, 9).

Since it will be confirmed later that trimethylacetic acid in CCl_4 solution exists only as monomer and cyclic dimer, the broadening of the 2970 cm^{-1} band is evidently not caused by the superposition of many sharper bands of a variety of species as suggested by Fénéant (12). Since repetitious spacings were found in the fine structures of the associated O-H stretching band from 2870 cm^{-1} to 2970 cm^{-1}, the band width broadening of associated acid may be explained in terms of the combination of other fundamental than O-H stretching, such as the very low frequency deformations of the H bond (3). It also leads to the interpretations of Davies and Evans (10) that the polymeric O-H stretching band consists of a series of different bands:

$$\nu_s(\text{polymer}) = \nu_s(\text{monomer}) - n\nu_\alpha$$

where ν_α is the H....O stretching mode.

The associated band around 2970 cm^{-1} region is badly overlapped by

CCl_4 absorption in 2.5 cm cell and C-H stretching; it is not possible to measure the optical densities of this band and therefore no dimer concentration can be calculated directly. The 3530 cm^{-1} non-associated O-H stretching band is also overlapped by the associated O-H stretchings if the acid concentration is high. Only solutions with concentrations lower than 4×10^{-3} M were measured so that a rather accurate measurement of optical density can be made.

The concentrations used and optical densities of the 3530 cm^{-1} band measured at various temperatures are listed in Table 3. The calculated ratios of concentration to optical density are also included. All values reported are the best values obtained or average values. In determining the I_o values, spectra of pure CCl_4 were used as base lines.

The concentrationsat various temperatures are calculated from the concentrations prepared at box temperature by using the equation $V_t = V_o(1 + \alpha t + \beta t^2 + \gamma t^3)$ given in the Handbook of Chemistry and Physics (17). Since the concentrations used are so low, only solvent density change with temperature is taken into consideration. The expansion of cell with increasing temperature is negligible compared to that of solutions.

C = O Stretching Mode. The typical spectra of C = O stretching of trimethylacetic acid in CCl_4 solution at various concentrations are shown in Fig. 4. The 5 mm rock salt cavity cell was used with the wedge cavity cell and pure CCl_4 in the reference beam. The spectra show two peaks at 1750 cm^{-1} and 1700 cm^{-1}. The ratio of optical density at 1750 cm^{-1} to acid concentration decreases with increasing acid concentration while

Table 3. Trimethylacetic acid in CCl_4 solution.
Optical density of non-associated O-H stretching at 3530 cm^{-1}.

Temperature (°C)	Concentration c x 10^3(M)	Optical density d (± 0.002)	c/d x 10^3(M)
	0.172	0.033	5.2
	0.429	0.053	8.1
11 ± 1	0.858	0.086	10.0
	1.716	0.127	13.5
	3.431	0.181	18.9
	0.167	0.043	3.9
	0.417	0.084	5.0
34 ± 1	0.834	0.136	6.16
	1.668	0.195	8.57
	3.336	0.303	11.0
	0.164	0.047	3.5
	0.409	0.111	3.67
50 ± 1	0.818	0.162	5.05
	1.635	0.278	5.89
	3.270	0.420	7.79
	0.186	0.039	4.8
	0.464	0.071	6.6
21.5 ± 1	0.928	0.103	8.99
	1.856	0.163	11.4
	3.713	0.235	15.8
	0.184	0.043	4.4
	0.461	0.076	6.1
26.5 ± 1	0.923	0.111	8.33
	1.845	0.168	11.0
	3.690	0.261	14.1

the ratio of optical density at 1700 cm^{-1} to acid concentration increases with increasing acid concentration. Therefore, the 1750 cm^{-1} band is assigned as non-associated C = O stretching band and the 1700 cm^{-1} band is assigned as associated C = O stretching band.

The concentrations used and optical densities of both the associated and non-associated C = O stretchings are listed in Table 4. The ratio of optical density to acid concentration for both non-associated and

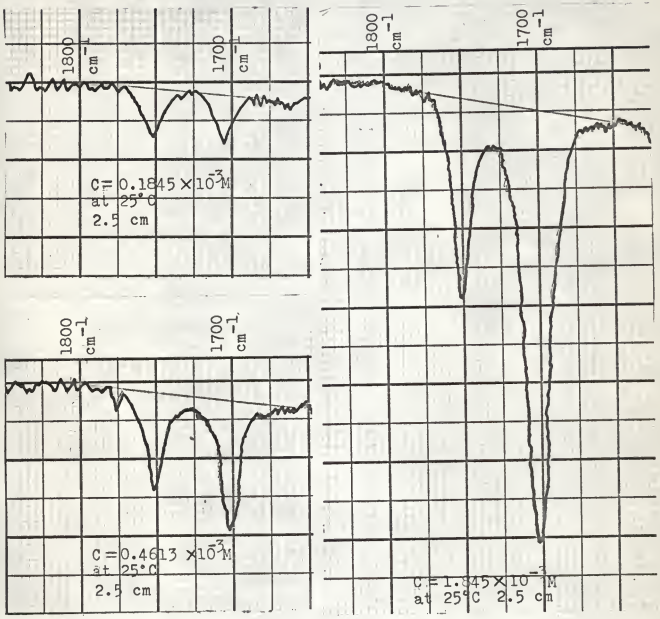


Fig. 4. C=O stretching of trimethylacetic acid in CCl_4 solution. Variation of absorption intensity with concentration.

Table 4. Trimethylacetic acid in CCl_4 solution.
Optical density of non-associated and associated C = O stretchings at 1750 cm^{-1} and 1700 cm^{-1}, respectively.
Temperature = 25 ± 1°C

Concentration C x 10^3(M)	Non-associated optical density d_1	d_1/c (M^{-1})	Associated optical density d_2	d_2/c (M^{-1})
0.185	0.035 ± 0.002	190	0.030 ± 0.003	160
0.463	0.066 ± 0.002	140	0.102 ± 0.003	221
0.927	0.103 ± 0.003	111	0.234 ± 0.003	253
1.853	0.163 ± 0.004	88.1	0.529 ± 0.015	286

associated stretching bands are also included. All the values reported are the best values obtained or the average values. In determining the I_o quantities, a straight tangent line was drawn at the base of each spectrum and this line was taken as the base line of the spectrum.

Since the C = O stretching intensity measurements are only for the purpose of checking the O-H stretching results, data were taken at only one convenient temperature.

Proton Magnetic Resonance

Chemical shifts can be reported in terms of the dimensionless quantity

$$\delta = \frac{Hr - H}{Hr} \times 10^6$$

where

H = resonance field of the compound of interest.

Hr = resonance field of a reference compound.

The chemical shifts of trimethylacetic acid are presented in terms of cycles per second, which can be converted to the dimensionless δ by dividing by the radiofrequency expressed in megacycles. Both the hydroxyl peak and the methyl peak are sharp singlets. The intensity of the methyl peak is about nine times stronger than that of the hydroxyl peak. Table 5 lists the chemical shifts of hydroxyl proton, measured by using the methyl peak as reference, as a function of concentration at various temperatures. All the values reported are the best values obtained or the average values. The hydroxyl chemical shift shows shifting to low field with increasing concentration. This low-field shift may be explained as follows (30):

"Normal hydrogen bonds are electronic in character. When a hydrogen bond, AH...B, is formed, the primary function of B is to provide a strong electric field in the vicinity of the A-H bond. The field tends to draw the proton away from the bonding electrons and consequently reduces the electron density immediately around it. This effect causes a reduction in screening and a shift to the low field."

CALCULATIONS AND RESULTS

Infrared Measurements

O-H Stretching Mode. The absorption intensities for the 3530 cm^{-1} band of trimethylacetic acid will be compared with the total acid concentrations. Table 6 lists the acid concentrations measured and the molar absorption coefficients calculated for each concentration, according to Beer's Law, at five temperatures.

Table 5. Trimethylacetic acid in CCl_4 solution.
Observed O-H chemical shift (cps at 60 Mc from methyl peak)

Concentration C(M)	$\frac{1}{\sqrt{c}}$	Observed O-H chemical shift ± 0.7 cps	Concentration C(M)	$\frac{1}{\sqrt{c}}$	Observed O-H chemical shift ± 0.7 cps
	11 ± 2°C			21.5 ± 2°C	
0.1392	2.680	653.5	0.1373	2.699	640.0
0.1880	2.306	662.2	0.1855	2.321	650.8
0.2097	2.184	664.0	0.2069	2.198	653.5
0.2571	1.972	666.8	0.2537	1.985	657.0
0.3072	1.804	670.0	0.3031	1.816	663.5
0.3900	1.601	674.0	0.3848	1.612	666.0
0.7841	1.129	679.0	0.7739	1.136	673.5
2.346	0.6531	685.8	2.315	0.6578	683.8
4.020	0.4987	687.2	3.968	0.5020	686.5
7.725	0.3598	693.5	7.624	0.3621	688.5
8.004	0.3536	693.0	7.899	0.3558	689.8
	34 ± 2°C			50 ± 2°C	
0.1354	2.718	630.7			
0.1828	2.338	638.2	0.1792	2.362	624.0
0.2040	2.213	642.8	0.1999	2.236	630.2
0.2500	2.000	649.5	0.2450	2.020	638.8
0.2988	1.829	656.3	0.2928	1.848	645.0
0.3792	1.623	659.4	0.3716	1.640	648.2
0.7625	1.145	663.8	0.7297	1.170	653.0
2.282	0.6622	677.5	2.238	0.6684	670.0
3.910	0.5058	682.0	3.834	0.5107	673.5
7.513	0.3649	683.0	7.368	0.3684	675.5
7.784	0.3584	683.3	7.634	0.3619	675.0

A plot of molar absorption coefficient versus acid concentration is shown in Fig. 5 for two temperatures. Obviously the molar absorption coefficient varies over the whole concentration range measured. Because no constant molar absorption coefficient is obtained, it is concluded that none of the solutions measured contains only monomer. An extrapolation to lower concentration is uncertain because the slope of the curve is still changing appreciably at the lowest concentrations at which accurate experimental measurements can be made. Therefore it is not possible to calculate monomer concentrations, and

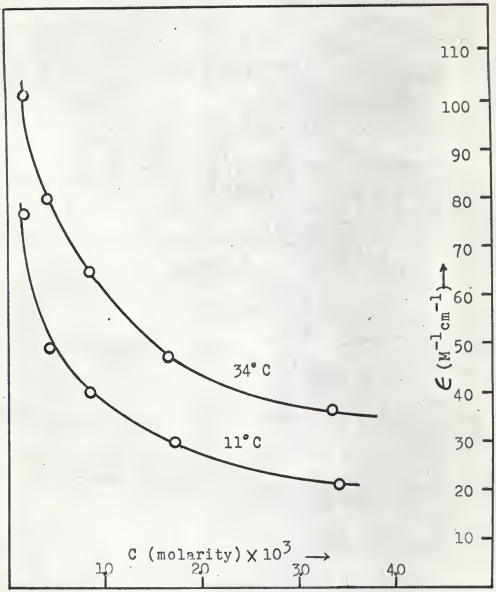


Fig. 5. O-H stretching vibration of trimethylacetic acid in CCl_4 solution. Variation of apparent molar absorption coefficient for the 3530 cm^{-1} band with acid concentration.

Table 6. Trimethylacetic acid in CCl_4 solutions.
Apparent molar absorption coefficient for the 3530 cm^{-1} band.

11+ 1°C		34 + 1°C		50 + 1°C		21.5 + 1°C		26.5 + 1°C	
Concentration $Cx10^3$(M)	Molar absorption coefficient ($M^{-1}cm^{-1}$)	Concentration $Cx10^3$(M)	Molar absorption coefficient ($M^{-1}cm^{-1}$)	Concentration $Cx10^3$(M)	Molar absorption coefficient ($M^{-1}cm^{-1}$)	Concentration $Cx10^3$(M)	Molar absorption coefficient ($M^{-1}cm^{-1}$)	Concentration $Cx10^3$(M)	Molar absorption coefficient ($M^{-1}cm^{-1}$)
0.172	77	0.167	102	0.164	114	0.186	83	0.184	91
0.429	49	0.417	80	0.409	109	0.464	61	0.461	66
0.858	40	0.834	65	0.818	79	0.928	44	0.923	48
1.716	29.6	1.668	47	1.635	68	1.856	35	1.845	36.4
3.431	21.2	3.336	36.4	3.270	51	3.713	25.4	3.690	28.4

consequently equilibrium constants, directly from the optical densities measured for the 3530 cm^{-1} band. However, the following analysis (16) can lead to the calculation of equilibrium constants.

If one assumes that the trimethylacetic acid-carbon tetrachloride system contains only monomers and cyclic dimers, then Beer's Law can be written as

$$d = \log \frac{I_o}{I} = \epsilon_M l C_M \quad \ldots \ldots (1)$$

where

d = optical density for the 3530 cm^{-1} band.

ϵ_M = molar absorption coefficient of monomer at 3530 cm^{-1}

C_M = monomer acid molar concentration.

Furthermore, by assuming the system is an ideal solution, the equilibrium constant for 2M (Monomer) $\rightleftharpoons$ D (dimer) can be written as $K = \frac{X_D}{X_M^2}$ according to the law of mass action. In dilute solution molarity is proportional to mole fraction, therefore, the equilibrium constant K can be expressed in terms of molarity.

$$K = \frac{C_D}{C_M^2} = \frac{C - C_M}{2 C_M^2} \quad \ldots\ldots (2)$$

where

C_M = molar concentration of monomer.

C_D = molar concentration of dimer.

C = molar concentration of total acid as prepared.

By combination of equation (1) and equation (2), one obtains

$$K = \frac{(C \epsilon_M l - d) \epsilon_M l}{2 d^2}$$

Rearranging gives

$$2d^2K = C\,\epsilon_M^2 l^2 - d\,\epsilon_M l$$

Dividing both sides by 2dK gives

$$d = \frac{\epsilon_M^2 l^2}{2K}\,\frac{C}{d} - \frac{\epsilon_M l}{2K} \quad \ldots\ldots (3)$$

Plots of d vs C/d are made in Fig. 6 at five temperatures. For each temperature a straight line is obtained. As concentration goes higher than 4×10^{-3}M, (the high concentration limit for the data in Fig. 6), the overlap of the 3530 cm^{-1} band by the bonded O-H band becomes serious and the plots start to deviate from straight lines.

From measuring the slope and intercept, one can calculate ϵ_M and consequently K by equations

$$\epsilon_M = \frac{\text{slope}}{(-\text{intercept})l} \quad \ldots\ldots (4)$$

and

$$K = \frac{\epsilon_M l}{2(-\text{intercept})} \quad \ldots\ldots (5)$$

Since the experimental data meet the requirement of a linear relationship between d and $\frac{c}{d}$ for the monomer $\rightleftharpoons$ cyclic dimer assumption, it may be concluded that trimethylacetic acid is a monomer $\rightleftharpoons$ cyclic dimer mixture in dilute CCl_4 solution.

Table 7 lists the equilibrium constants calculated by the least squares method. All values reported are the best values obtained or average values.

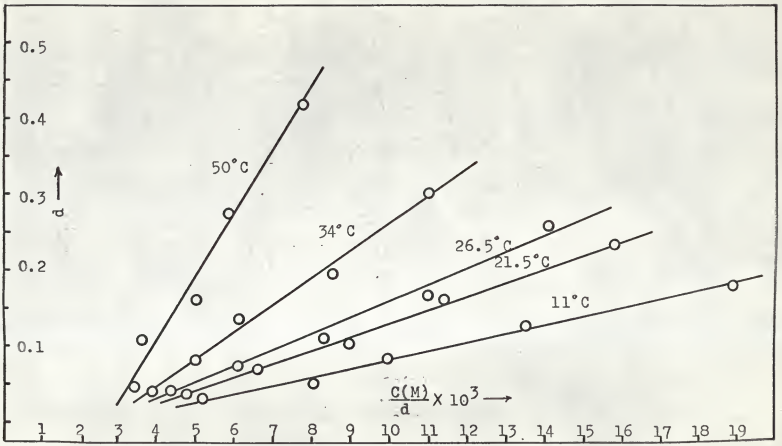


Fig. 6. O-H stretching vibration of trimethylacetic acid in CCl_4 solution. Relation of optical density, d, to the ratio, C/d, of the total acid concentration to the optical density.

Table 7. Trimethylacetic acid in CCl_4 solution.
Monomer $\rightleftharpoons$ cyclic dimer equilibrium constants evaluated from the O-H stretching mode.

Temperature (°C)	(°K)	$10^3/T(°K)$	Molar absorption coefficient (cm^{-1} M^{-1})	Equilibrium constant $K(M^{-1})$	log K
11 ± 1	284 ± 1	3.52	155 ± 7	6800 ± 200	3.832
21.5 ± 1	294.5 ± 1	3.40	145 ± 7	3520 ± 180	3.546
26.5 ± 1	299.5 ± 1	3.34	139 ± 7	2750 ± 150	3.439
34 ± 1	307 ± 1	3.26	152 ± 7	2040 ± 150	3.310
50 ± 1	323 ± 1	3.10	147 ± 7	830 ± 150	2.919

C = O Stretching Mode. As Table 4 shows, the optical densities of both the associated and non-associated C = O stretchings can be measured. Again, if one assumes that the trimethylacetic acid - carbon tetrachloride system contains only monomers and cyclic dimers, Beer's Law can be written as (8)

$$d_1 = C_1 \epsilon_1 l \quad \ldots\ldots (6)$$

$$d_2 = C_2 \epsilon_2 l \quad \ldots\ldots (7)$$

where

d_1 and d_2 are the optical densities at 1750 cm^{-1} and 1700 cm^{-1}, respectively.

C_1 and C_2 are monomer and dimer concentrations, respectively.

ϵ_1 and ϵ_2 are molar extinction coefficients of monomer and dimer at 1750 cm^{-1} and 1700 cm^{-1}, respectively.

l is the cell length.

If d_2 is divided by d_1, one can get

$$\frac{d_2}{d_1} = \frac{\epsilon_2}{\epsilon_1}\frac{C_2}{C_1} = \frac{\epsilon_2}{\epsilon_1}\frac{C-C_1}{2C_1} \quad \ldots\ldots (8)$$

Substituting C_1 from equation (6) into equation (8) and rearranging, it becomes

$$\frac{d_2}{C} = \frac{1}{2}\epsilon_2 l - \frac{1}{2}\frac{\epsilon_2}{\epsilon_1}\frac{d_1}{C} \quad \ldots\ldots (9)$$

A plot of $d_{2/c}$ versus $d_{1/c}$ is shown in Fig. 7. From measuring the slope one can obtain the ratio of molar absorption coefficients ϵ_2/ϵ_1. Once the ratio ϵ_2/ϵ_1 is known, the monomer concentration C_1 can be calculated from d_1 and d_2 measurements. By rearranging equation (8), it becomes

$$C_1 = \frac{C\,\frac{d_1}{d_2}\,\frac{\epsilon_2}{\epsilon_1}}{2 + \frac{d_1}{d_2}\,\frac{\epsilon_2}{\epsilon_1}} \quad \ldots\ldots (10)$$

Substituting $KC_1 = \frac{C - C_1}{2C_1}$ into equation (8) and rearranging it, one can get

$$K = \frac{1}{C_1}\frac{d_2}{d_1}\frac{\epsilon_1}{\epsilon_2} \quad \ldots\ldots (11)$$

The equilibrium constant, K, can thus be calculated from equation (11) for each concentration measured.

As Fig. 7 shows, the experimental data meet the linear relationship between $d_{2/c}$ and $d_{1/c}$ as derived from the assumption that trimethylacetic

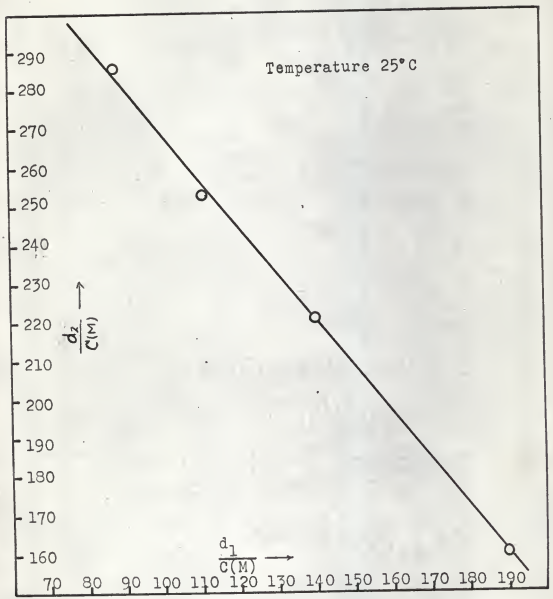


Fig. 7. C=O stretching vibration of trimethylacetic acid in CCl_4 solution. Relation of the intensity of dimer band near 1700 cm^{-1}/total acid concentration, d_2/C, to the intensity of monomer band near 1750 cm^{-1}/total acid concentration, d_1/C.

acid is a monomer $\rightleftharpoons$ cyclic dimer mixture in CCl_4 solution; the monomer $\rightleftharpoons$ cyclic dimer equilibrium is also supported by the C = O stretching mode.

Equilibrium constants evaluated from C = O stretching are listed in Table 8. All values reported are the best values obtained or average values.

Table 8. Trimethylacetic acid in CCl_4 solution.
Monomer $\rightleftharpoons$ cyclic dimer equilibrium constants evaluated from C = O stretching.

$\frac{\epsilon_2}{\epsilon_1} = 2.5$ Temperature = 25 ± 1°C

Acid concentration C x 10^3(M)	Ratio of optical densities (d_1/d_2)	Monomer concentration C_1 x 10^3(M)	Equilibrium constant K (M^{-1})
0.185	1.2	0.110	3100 ± 300
0.463	0.66	0.210	3000 ± 250
0.927	0.441	0.332	2740 ± 150
1.853	0.340	0.518	2500 ± 150

Proton Magnetic Resonance Measurements

Again, by assuming that trimethylacetic acid has only monomers and cyclic dimers present in CCl_4 solution, the observed O-H chemical shift, δ_{obs}, can be expressed by equation (12) as a weighted average of the chemical shifts of the species present (36)

$$\delta_{obs} = \alpha_1 \delta_1 + \alpha_2 \delta_2 \quad \ldots\ldots (12)$$

where

α_1 is the fraction of monomers.

α_2 is the fraction of dimers.

δ_1 is the O-H chemical shift of monomer.

δ_2 is the O-H chemical shift of dimer.

The monomer and dimer fractions can be written as

$$1 = \frac{C_1}{C} = \frac{C_1}{C_1 + 2C_2} \quad \ldots\ldots (13)$$

$$2 = \frac{2C_2}{C} = \frac{2C_2}{C_1 + 2C_2} \quad \ldots\ldots (14)$$

Now, by solving $C = C_1 + 2C_2$ and $K = \frac{C_2}{C_1^2}$ for C_1 and C_2, one can obtain

$$C_1 = \frac{\sqrt{1 + 8KC} - 1}{4K} \quad \ldots\ldots (15)$$

$$C_2 = \frac{4KC - \sqrt{1 + 8KC} + 1}{8K} \quad \ldots\ldots (16)$$

By substituting equation (15) into equation (13), and equation (16) into equation (14), one obtains

$$\alpha_1 = \frac{\sqrt{1 + 8KC} - 1}{4KC}$$

$$\alpha_2 = 1 - \frac{\sqrt{1 + 8KC} - 1}{4KC}$$

The observed O-H chemical shifts can then be written as equation (17) if one substitutes the δ_1 and δ_2 into equation (12).

$$\delta_{obs} = \delta_2 + (\delta_1 - \delta_2) \frac{\sqrt{1 + 8KC} - 1}{4\,KC} \quad \ldots\ldots (17)$$

Figure 8 shows a plot of observed O-H chemical shifts versus concentrations at four temperatures. As concentration increases, δ_{obs} shows shifting toward low field until a certain concentration, after which the δ_{obs} is independent of concentration. The horizontal region of the curve may be explained as the region in which all of the acid molecules are completely dimerized so that chemical shift no longer varies with concentration. Thus, dimer O-H chemical shift, δ_2, can be obtained experimentally.

The dilute region shows δ_{obs} changing rapidly with concentration. Accurate chemical shift measurements can not be made for more dilute solutions because of the sensitivity limitations of the NMR instrument. An extrapolation to lower concentration will be inaccurate because the slope of the curve is still changing appreciably at the lowest concentration at which accurate experimental measurements can be made.

A least squares iteration method shown below has been used to solve for the equilibrium constant, K, and monomer chemical shift, δ_1, from equation (17).

(1) Express $\delta = B + Ay$

(2) Guess a K value and calculate the y's from $y = \frac{\sqrt{1 + 8KC} - 1}{4\,KC}$ for all concentrations measured.

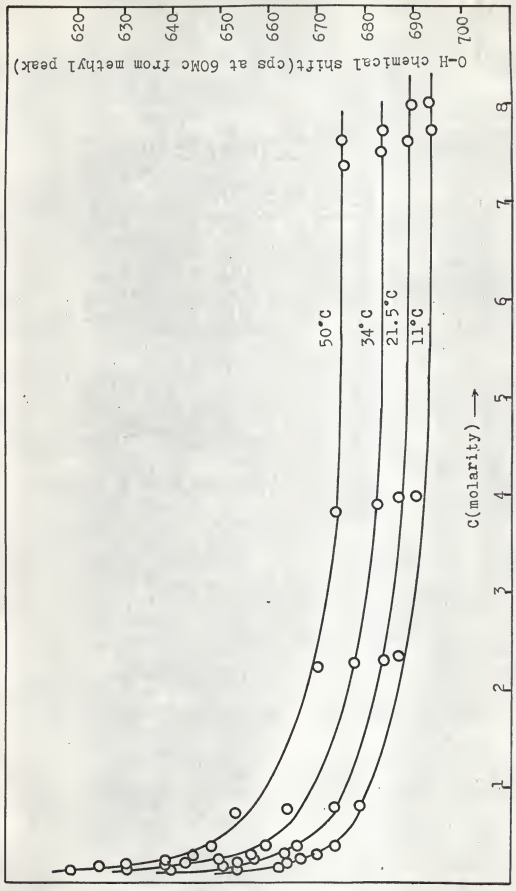


Fig. 8. Trimethylacetic acid-CCl_4. Variation of observed O-H chemical shift with concentration.

(3) Obtain A and B from the method of least square

$$A = \frac{\left(\sum_{i=1}^{n} \delta_i\right)\left(\sum_{i=1}^{n} y_i\right) - n\left(\sum_{i=1}^{n} \delta_i y_i\right)}{\left(\sum_{i=1}^{n} y_i\right)^2 - n\left(\sum_{i=1}^{n} y_i^2\right)}$$

$$B = \frac{\left(\sum_{i=1}^{n} \delta_i y_i\right)\left(\sum_{i=1}^{n} y_i\right) - \left(\sum_{i=1}^{n} \delta_i\right)\left(\sum_{i=1}^{n} y_i^2\right)}{\left(\sum_{i=1}^{n} y_i\right)^2 - n\left(\sum_{i=1}^{n} y_i^2\right)}$$

(4) Justify whether the guessed K value is the equilibrium constant by $D = (\delta_2 - B)^2$. The guessed K value will be the equilibrium constant if D is equal to zero or very close to zero.

(5) Monomer O-H chemical shift can then be calculated from A after equilibrium constant is obtained satisfactorily.

A Fortran computer program has been written and run on the IBM 1620 computer, but no good results have been obtained. The output values of D showed just a very insensitive convergence for K values tried ranging from 10^2 to 10^{40} if high concentrations were included in the computation. If only dilute concentrations were used in the computation, the output values of D showed irregular behavior for the all K values tried. Experimental error and the necessity of subtracting quantities of like order of magnitude could cause these poor results.

Also a graphic method has been attempted for finding K and δ_1. The δ_{obs}'s were plotted versus y values calculated from a guessed K value. Straight lines were expected only when the K value guessed is the equilibrium

constant. However, as Fig. 9 shows, all of the lines are linear in the dilute region regardless of the K values. This unexpected phenomenon becomes clear if one considers the following possible approximation.

From the IR results one knows that the equilibrium constants are of the order of 10^3. The concentrations used in the PMR measurements are higher than 0.1 M because of the sensitivity limitations of the instrument. Therefore, y can be simplified by considering $8KC \gg 1$.

$$y = \frac{\sqrt{1 + 8KC} - 1}{4\,KC} \cong \frac{\sqrt{8\,KC}}{4\,KC} = \frac{1}{\sqrt{2\,KC}} \quad \ldots\ldots (18)$$

substituting equation (18) into equation (17), one can get

$$\delta_{obs} = \delta_2 + \frac{(\delta_1 - \delta_2)}{\sqrt{2\,K}} \qquad \frac{1}{\sqrt{C}} \quad \ldots\ldots (19)$$

Since δ_2 and δ_1 are constants, different values of K can only change the slope, but not the linearity in the δ_{obs} versus y plot.

Although the equilibrium constant has not been obtained from this graphical treatment, one should recognize that the conclusion that trimethylacetic acid exists in CCl_4 as only monomer and cyclic dimer is also supported by the PMR measurements, because the experimental data meet the requirement of a linear relationship between δ_{obs} and y (i.e. $1/\sqrt{C}$) as derived from the original assumption of only monomers and cyclic dimers being present in CCl_4 solution.

If one makes a combined use of IR and PMR by employing the equilibrium constants obtained from IR measurements, the monomer O-H chemical shifts can then be calculated from the slopes of δ_{obs} versus $\frac{1}{\sqrt{C}}$ plots.

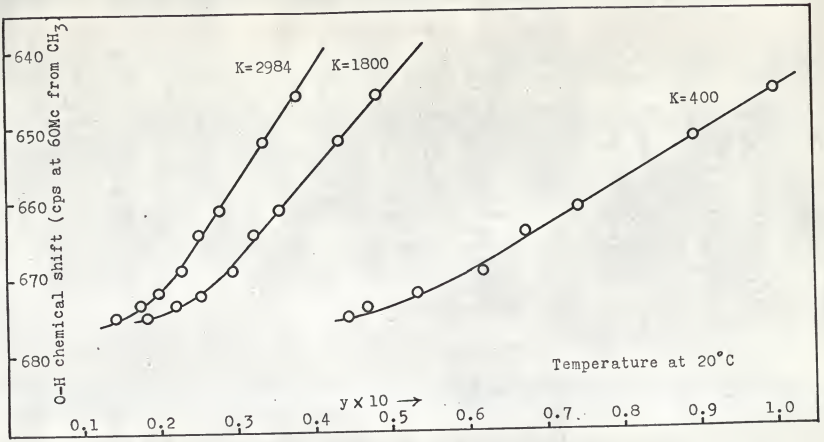


Fig. 9. Trimethylacetic acid in CCl_4 solution. The relation of observed O-H chemical shift to $y=(\sqrt{1+8KC}-1)/4KC$ for various guessed monomer⇌dimer equilibrium constants.

$$\text{slope} = \frac{\delta_1 - \delta_2}{\sqrt{2K}}$$

Rearranging gives

$$\delta_1 = \delta_2 + \sqrt{2K} \times (\text{slope}) \quad \ldots\ldots \quad (19)$$

Some data included in Table 5 are plotted in Fig. 10.

Table 9 lists the calculated monomer O-H chemical shifts as well as the experimental dimer O-H chemical shifts at various temperatures. Slopes used in the calculations are obtained from least squaresmethod. All values reported are the best values obtained or average values.

Table 9. Trimethylacetic acid in CCl_4 solution. Monomer and dimer O-H chemical shifts (cps at 60 Mc from methyl peak).

Temperature °C	Monomer O-H chemical shift δ_1 (cps)	Dimer O-H chemical shift δ_2 (cps)*
11 ± 2	-1490 ± 150	693 ± 5
21.5 ± 2	-1430 ± 150	690 ± 10
34 ± 2	-1220 ± 150	683 ± 10
50 ± 2	-1090 ± 200	675 ± 25

*The values are from experiment with errors of ± 2 cps. The deviations shown give the difference between experimental values and extrapolated values in Fig. 10.

A negative shift indicates that measured peak is at a higher applied magnetic field (lower cps) than the reference peak from which the shift is measured. The uncertainty of δ_1 includes the experimental errors of the equilibrium constant measurements.

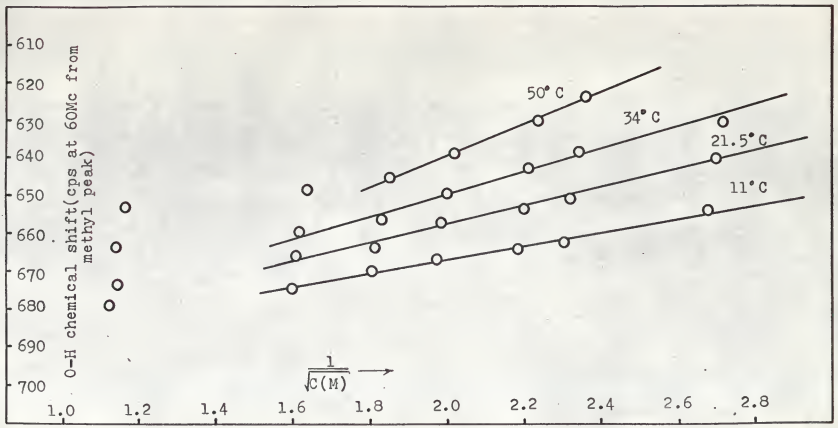


Fig. 10. Trimethylacetic acid in CCl_4 solution. Relation of observed O-H chemical shift to reciprocal of the square root of concentration.

The Calculation of Changes in Standard Enthalpy, Free Energy, and Entropy for Hydrogen Bond Formation

The thermodynamic functions can be calculated by assuming that the ideal associated solution model (33) is valid in the trimethylacetic acid - CCl_4 system. The thermodynamic equilibrium constant for a process in solution is defined in terms of the equilibrium values of the activities of the individual species involved. Since activity may be expressed as the product of mole fraction and activity coefficient, the ideal associated solution consists of species whose activities equal their mole fractions because activity coefficients are unity by definition in the ideal associated solution.

The change in standard enthalpy, ΔH^o, can be calculated from the thermodynamic equilibrium constant and its variation with temperature. Usually it can be written as

$$\log K = -\frac{\Delta H^o}{2.303R} \quad \frac{1}{T} + \text{constant}$$

This relation is based on the assumption that ΔH^o is temperature independent over the temperature range considered. By introducing the gas constant R = 1.987 cal/deg. mole, the relation becomes

$$\log K = \frac{-\Delta H^o}{4.576} \quad \frac{1}{T} + \text{constant}$$

Figure 11 shows the plot of log K versus $\frac{1}{T}$ for the values included in Table 7. From measuring the slope one can calculate that the standard enthalpy for hydrogen bond formation of trimethylacetic acid in CCl_4 is $\Delta H_2^o = -9.55 \pm 0.5$ kcal/mole dimer.

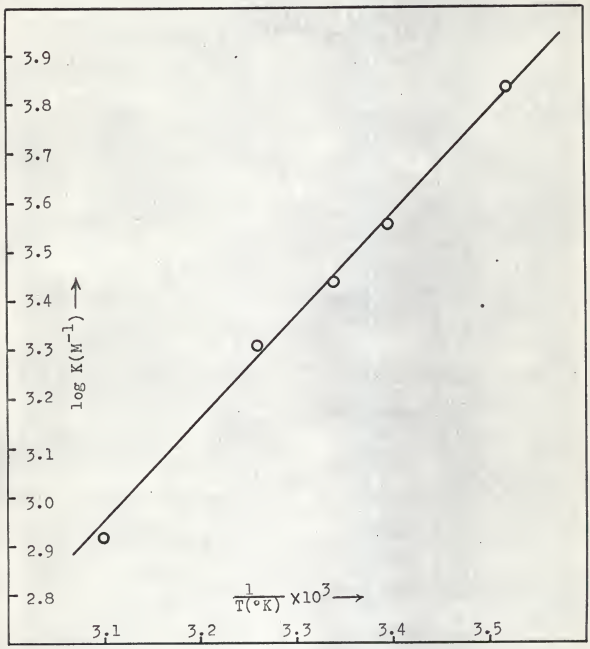


Fig. 11. Relation of logK to 1/T. Trimethylacetic acid in CCl_4 solution. Equilibrium constants, K, are evaluated from quantitative measurements of the intensity of free O-H band at 3530 cm^{-1}.

The equilibrium constant in molarity units is used in the ΔH° calculation because in dilute solution molarity is proportional to mole fraction and the units of K do not influence the value of ΔH°. Since the units of K influence both ΔG° and ΔS°, equilibrium constants obtained in molarity will be converted to mole fraction by using the equation

$$K_x = K_c V_o^{\Delta n}$$

where

V_o = volume per mole of solution, approximately equal to the molar volume of the pure solvent.

Δn = the increase in number of moles. For

$$2M \rightleftharpoons D, \quad \Delta n = -1$$

Changes in standard free energies calculated from $\Delta G^{\circ} = -RT \ln K_x$ as well as standard entropies calculated from $\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T}$ are listed in Table 10.

DISCUSSION

Monomer $\rightleftharpoons$ Cyclic Dimer

The equilibrium constants, and consequently thermodynamic functions and monomer O-H chemical shifts, calculated from the O-H stretching mode data are based on the assumption that the absorption at 3530 cm^{-1} is due to the monomer species only. This can be true only if dimeric acid or any other species does not absorb at this frequency.

Smith and Creitz (35) found that sterically hindered alcohols such as 2,4-dimethyl-3-ethyl-3-pentanol exhibit a narrow absorption for free

Table 10. Trimethylacetic acid in CCl_4 solution.
Thermodynamic functions for hydrogen bond formation.

Temperature °K	Equilibrium constant $K_X \times 10^{-4}$ (X^{-1})	Standard enthalpy ΔH^o Kcal/mole dimer	Standard free energy $-\Delta G^o$ Kcal/mole dimer	Standard entropies $-\Delta S^o$ cal/deg-mole dimer
284 ± 1	7.13 ± 0.21		6.30 ± 0.04	11.45 ± 1.9
294.5 ± 1	3.64 ± 0.19		6.15 ± 0.04	11.52 ± 1.7
299.5 ± 1	2.83 ± 0.17	-9.55 ± 0.5	6.12 ± 0.06	11.45 ± 1.9
307 ± 1	2.08 ± 0.16		6.07 ± 0.06	11.35 ± 1.8
323 ± 1	0.83 ± 0.18		5.80 ± 0.15	11.60 ± 2.0

O-H stretching with a lower frequency shoulder. As the concentration of alcohol increases, the lower frequency shoulder becomes the dominant absorption and a shoulder appears at higher frequency. This result was thought to be due to the presence of the terminal O-H group of a linear dimer. There are no such shoulders found for the 3530 cm^{-1} band in the trimethylacetic acid - CCl_4 system.

Trimethylacetic acid has been shown, by both IR and PMR methods, to consist of only monomers and cyclic dimers in dilute carbon tetrachloride solution, therefore, there should be no terminal free O-H absorption at the 3530 cm^{-1} band. The result $\Delta H_2^o = -9.55 \pm 0.5$ kcal/mole dimer provides additional support for the conclusion that the dimer is cyclic with two hydrogen bonds per mole of dimer since hydrogen bonds of the O-H . . . O = C type in non-polar solvents are expected (28) to have ΔH^o values between 4 and 6 kcal/mole of bond.

In the plot of optical density, d, versus ratio of acid concentration to optical density, c/d, the experimental data deviate from linearity if the acid concentration is higher than 4×10^{-3}M. This may cause one to doubt the validity of monomer $\rightleftharpoons$ cyclic dimer equilibrium. However, since the PMR results also support the monomer $\rightleftharpoons$ cyclic dimer equilibrium in the more concentrated region, the problem can be explained as the influence of associated O-H stretching band because at higher acid concentrations the broad absorption characteristic of hydrogen bonded O-H stretching begin to overlap the free O-H band, and consequently the determination of Io becomes less accurate. Because of the limited amount of monomer present in the more concentrated solutions, slight errors in the Io determinations, and consequently in the intensity measurements, are

capable of causing significant deviations from linearity in the plots of d versus $c/_d$ and consequently poorer equilibrium constant values. When the acid concentration is higher than 0.4 M, the PMR data plots of δ obs versus $1/\sqrt{c}$ also show deviation from linearity, but this phenomenon can be explained in terms of the effect of activity coefficients because the solution is too concentrated to behave as an ideal associated solution (33) in this region. An additional difficulty is that molarity and mole fraction are no longer simply related by a factor that is concentration-independent and consequently a plot vs $1/\sqrt{c}$ in molarity units is no longer appropriate since the presence of $1/\sqrt{2K}$ in the slope can no longer make $1/\sqrt{2KC}$ the same for both molarity and mole fraction units.

Effect of Solvent and Temperature

Solvent is one of the variables with an important influence on the IR and PMR spectra of substances which form hydrogen bonds. Many solvents can participate in the associations and thus produce new hydrogen bonding equilibria involving the solvents. These additional equilibria may furnish an interfering factor in the spectra with which one may be interested in measuring optical density or chemical shift and then calculating equilibrium constants and thermodynamic functions.

Liddel and Becker (20) have made a quantitative study of the intensity of absorption of CH_3OH in the 3640 cm^{-1} region as a function of concentration in CCl_4 and as a function of temperature. They found that the peak intensity of the free O-H band in dilute solution (0.005M) is strongly dependent on temperature. The intensity decreases nearly 50% over the temperature range -10° to +50°C and is accompanied by a slight increase

in frequency (ca 6 cm^{-1}). Since the alcohol molecules in 0.005M solution have been confirmed to be in the monomolecular state, the significant intensity variation of the 3640 cm^{-1} band implies that the O-H group interacts with CCl_4 in a fashion that influences the intensity of the stretching mode and which is very temperature sensitive.

Hammaker (15) has measured the intensity for the 7133 cm^{-1} band of methanol in CCl_4 solution as a function of temperature at 0.00491M. He found a fractional rate of change of the absorption coefficient with temperature of -3.0×10^{-3} deg^{-1}. The variation of the intensity with temperature is accounted for by collisional perturbation (7.) by the solvent, CCl_4.

The absorption coefficient results in Table 7 for the 3530 cm^{-1} band are not sufficiently accurate to warrant speculation about their possible temperature variation. The monomer O-H chemical shift of trimethylacetic acid in CCl_4 solution calculated in this research also shows variation with temperature. So does the measured dimer O-H chemical shift, though to a less degree. It seems highly probable that this is a specific interaction of trimethylacetic acid with CCl_4 analogous to hydrogen bonding and might be considered as a weak type of hydrogen bonding to the solvent.

Pitzer and Davis (11) have measured the monomer and dimer chemical shifts for acetic acid in benzene solution at several temperatures. Their results are compared to the results of this research in Fig. 12, a plot of monomer and dimer chemical shift as a function of absolute temperature and in Fig. 13, a plot of chemical shift versus reciprocal absolute temperature. For the monomer chemical shift the data of this research

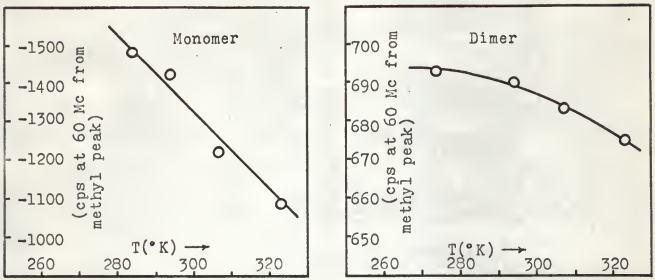


Fig. 12a. Trimethylacetic acid in CCl_4 solution. Relation of monomer and dimer O-H chemical shift to temperature.

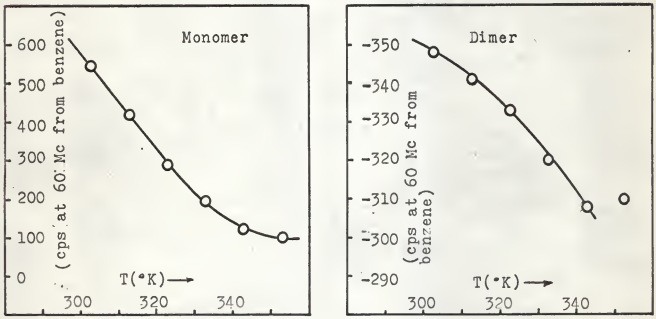
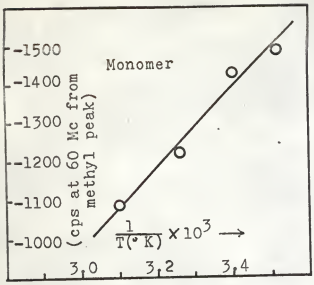


Fig. 12b. Acetic acid in benzene solution. Relation of monomer and dimer O-H chemical shift to temperature. (data from Davis and Pitzer, J. Phys. Chem., 64, 888(1960))

* For trimethylacetic acid a negative chemical shift value corresponds to an up field shift, for acetic acid a negative chemical shift value corresponds to a down field shift.



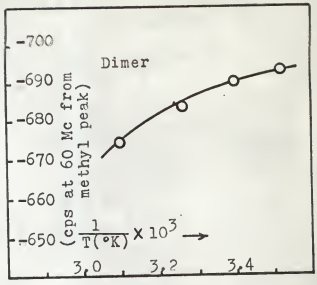
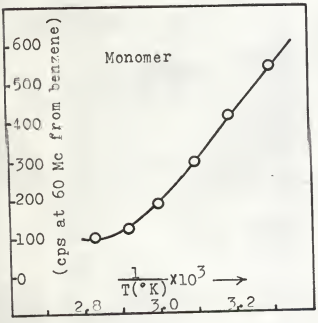


Fig. 13a. Trimethylacetic acid in CCl_4 solution. Relation of monomer and dimer O-H chemical shift to reciprocal of the absolute temperature.



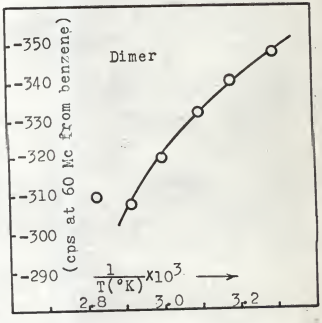


Fig. 13b. Acetic acid in benzene solution. Relation of monomer and dimer O-H chemical shift to reciprocal of the absolute temperature.

* For trimethylacetic acid a negative chemical shift value corresponds to an up field shift, for acetic acid a negative chemical shift value corresponds to a down field shift.

give linear relations with both T and $1/T$, probably due to experimental uncertainty and the narrow temperature range covered. For the monomer chemical shift the data of Davis and Pitzer give non-linear curves for both T and $1/T$; however, both plots are linear over the range which overlaps part of the temperature range of this research. For the dimer chemical shifts, both the data of Davis and Pitzer and that of this research give non-linear relations with both T and $1/T$. For the data of this research, a negative chemical shift value corresponds to an up-field shift, but for the data of Davis and Pitzer a negative chemical shift value corrsponds to a down-field shift. In both sets of data the monomer chemical shifts move down-field with increasing temperature; however, the dimer chemical shifts move up-field with increasing temperature. This similar behavior of the monomer chemical shift for the two solvents implies that the interaction between the carboxyl group and the solvent is of the same kind for both solvents. The fact that the slope in the $1/T$ plot is slightly larger for benzene as the solvent implies that the interaction energy of the carboxyl group with the solvent is slightly larger for benzene. All these results are consistent with the existence of a hydrogen bonding interaction between the carboxyl group and the solvent.

It is generally accepted that the temperature effect on peak intensity reveals the shift in equilibria involving a variety of species, each with a characteristic absorption coefficient (20, 21). However it has been suggested by Finch and Lippincott (13) that both the O-H stretching frequency and the absorption coefficient of each particular hydrogen bonded species may change with temperature. They found that the increase in frequency and the decrease in intensity are proportional to the

absolute temperature for isopropyl alcohol and n-butyl alcohol over a temperature range 207 to 298 °K. Liddel and Becker (21) have measured the apparent absorption coefficient for the 3635 cm^{-1} (monomer) band of ethanol over the temperature range -15 to 60°C at concentration 0.005 M. They reached the same conclusion that absorption coefficient decreases with increasing temperature.

A variation in absorption coefficients would have serious impact on the spectroscopic measurements of thermodynamic properties if the temperature variation were not taken into account. In this research on trimethylacetic acid, the correction for temperature dependence of absorption coefficient has been made because equilibrium constants are calculated from absorption coefficients evaluated at the individual temperatures used.

The Equilibrium Constants and Thermodynamic Functions

The monomer $\rightleftharpoons$ cyclic dimer equilibrium constants of trimethylacetic acid in CCl_4 evaluated by using both the O-H stretching mode and C = O stretching mode show good agreement. The average values obtained from the O-H stretching mode at 26.5°C and the C = O stretching mode at 25°C are 2750 $\pm$ 150 (Table 7) and 2835 $\pm$ 210 (Table 8), respectively. Furthermore, the values from C = O stretching mode also seem reasonable as compared to the values Chang and Morawetz (8) reported:

Trimethylacetic acid in CCl_4 at 29.6°C

Concentration	Equilibrium constant
C x 10^3 (M)	Ka (M^{-1})
3.16	2130
6.32	1920
12.64	1640
19.0	1230

The log K versus $1/T$ plot in Fig. 11 for the O-H stretching data predicts K = 2400 ± 150 M^{-1} for the concentration range up to 4 x 10^{-3} M at 29.6°C. This value is to be compared to the lowest concentration of Chang and Morawetz due to the concentration effect. However, one should keep in mind that the effect of solvent, as previously discussed, may have influence on the accuracy of equilibrium constant and consequently the thermodynamic functions.

Barrow and Yerger (4) have measured the equilibrium constants of acetic acid in CCl_4 over a concentration range 0.186 x 10^{-3} to 0.349 M. The association constants they reported increase by a factor of about two with a decrease in concentration by a factor of about 500. The equilibrium constants of trimethylacetic acid in CCl_4 solution evaluated from C = O stretching in this research also exhibit the same tendency that equilibrium constant increases as concentration decreases (Table 8).

The equilibrium constant of trimethylacetic acid in CCl_4 solution has not been found by PMR measurements of O-H chemical shift. The problem lies in the difficulty of measuring the monomer O-H chemical shift because of the sensitivity limitation of instrument. However,

if the PMR instrument can measure the average chemical shift of solution as low as 10^{-3} M, the approximation of $8Kc >> 1$ will no longer be true and the monomer percent will be higher and equilibrium constant may be calculated by the graphical or the least squares methods described in this research.

Huggins, et al. (18) have shown that at infinite dilution the slope of the observed chemical shift, δ_{obs}, versus mole fraction, x, curve is given by the equation

$$\left(\frac{\partial \delta}{\partial x}\right)_{x=0} = 2K(\delta_M - \delta_D)$$

It is thus possible to evaluate the equilibrium constant if δ_M, δ_D and the slope at infinite dilution are known. The δ_M is the limiting value of δ_{obs} at infinite dilution and $\left(\frac{\partial \delta}{\partial x}\right)_{x=0}$ is the slope of the curve extraplated to x = o.

The behavior of δ_{obs} as a function of concentration for trimethylacetic acid in CCl_4 solution at various temperatures has been shown in Fig. 8. It can be seen that the $\left(\frac{d\delta}{dx}\right)$ is still changing rapidly at the lowest concentrations at which accurate experimental measurements can be made. Therefore, neither the monomer O-H chemical shift nor the equilibrium constant can be obtained by this method.

A large number of equilibrium constants for various hydrogen bonding species have been reported. A common problem is the lack of real knowledge of the species present in the system (29). Generally, in order to avoid this problem, it is necessary to use a concentration range sufficiently

low so that only monomer and one polymer are the important species. This is a condition difficult to meet sometimes. In this research, the rather bulky trimethylacetic acid is investigated. As the plot of observed O-H chemical shift versus acid concentration shows, it is reasonable to believe that the dimer is the only polymer species present in the trimethylacetic acid - CCl_4 system because the observed O-H chemical shift does not show significant change over a wide high concentration range.

The thermodynamic functions for the dimerization of trimethylacetic acid in dilute CCl_4 solution shown in Table 10 are in reasonable agreement with available literature data for the dimerization of carboxylic acids in CCl_4 and in benzene as measured by both spectroscopic and non-spectroscopic methods. The result $\Delta H_2^\circ = -9.55 \pm 0.5$ kcal/mole dimer is in good agreement with the recent measurement of Affsprung, Christian, and Melnich (2) for acetic acid in CCl_4 $\Delta H_2^\circ = -10.7 \pm 1.2$ kcal/mole dimer and falls within the range of values for a single hydrogen bond of -4.0 to -5.5 kcal/mole of bond obtained (28) for a number of substituted and non-substituted aliphatic and aromatic carboxylic acids in CCl_4 or benzene solution provided that the dimer is taken to be cyclic. This result does not support the suggestion of Bellancy et al. (6) that the broadness of the dimer O-H stretching band is due to overlap of bonded bands for both cyclic and linear dimers. The agreement between the equilibrium constants obtained in this research and literature values will carry over to the ΔG° values.

The result $-\Delta S^\circ = 11.5 \pm 2$ e.u. is in the range of 7 - 21 e.u. reported (28) for aromatic carboxylic acids in CCl_4 or benzene solution.

CONCLUSIONS

The important results of this research may be summarized as follows:

(1) The trimethylacetic acid-carbon tetrachloride system has been confirmed to have a monomer $\rightleftharpoons$ cyclic dimer equilibrium.

(2) The equilibrium constants of trimethylacetic acid in CCl_4 solution have been evaluated at 11°, 21.5°, 26.5°, 34° and 50°C over a concentration range 0.00018 to 0.0040 M by quantitative measurements of the intensity of the sharp O-H band at 3530 cm^{-1}. The results have been checked by using the C = O stretching bands at 1750 and 1700 cm^{-1} at 25°C over the same concentration range.

(3) The changes in standard enthalpy, free energy and entropy for dimer formation of trimethylacetic acid in CCl_4 solution have been evaluated at 11°, 21.5°, 26.5°, 34° and 50°C.

(4) The monomer and dimer O-H chemical shifts of trimethylacetic acid in CCl_4 solution have been evaluated at 11°C, 21.5°C, 34°C and 50°C and a significant temperature effect has been noted.

ACKNOWLEDGMENT

The author wishes to express his appreciation to his major professor, Dr. Robert M. Hammaker, for his willingness to encourage and direct this research.

The author is indebted to the Department of Chemistry, Kansas State University, for the necessary assistance to this research.

LITERATURE CITED

1. Arnold, J. T., and H. G. Packard. Variations in absolute chemical shift of nuclear induction signals of hydroxyl groups of methyl and ethyl alcohol. J. Chem. Phys., 19, 1608 (1951).

2. Affsprung, H. E., S. D. Christian, and A. M. Melnick. Heterodimerization of acetic and trichloroacetic acids in CCl_4 solution. Spectrochim. Acta., 20, 285 (1964).

3. Badger, R. M., and S. H. Bauer. The spectrum characteristic of hydrogen bonds. J. Chem. Phys., 5, 369 (1937).

4. Barrow, G. M., and E. A. Yerger. The dimerization of acetic acid in carbon tetrachloride and chloroform. J. Am. Chem. Soc., 76, 5248 (1954).

5. Becker, E. D., U. Liddel, and J. N. Shoolery. Nuclear magnetic resonance studies of hydrogen bonding in ethanol. J. Molec. Spectroscopy, 2, 1 (1958).

6. Bellamy, L. J., R. F. Lake, and R. J. Pace. Hydrogen bonding in carboxylic acids--monocarboxylic acids. Spectrochim. Acta., 19, 443 (1963).

7. Brown, T. L. Kinetic interpretation of the temperature dependence of infrared absorption. J. Chem. Phys., 24, 1281 (1956).

8. Chang, S. Y., and H. Morawetz. Polymer association. Molecular aggregation. J. Phys. Chem., 60, 782 (1956).

9. Coggeshall, N. D. Electrostatic interaction in hydrogen bonding. J. Chem. Phys., 18, 978 (1950).

10. Davies, M., and J. C. Evans. The association band of the hydrogen bridge. J. Chem. Phys., 20, 342 (1952).

11. Davis, J. C., and K. S. Pitzer. Nuclear magnetic resonance studies of hydrogen bonding. Carboxylic acids. J. Phys. Chem., 64, 886 (1960).

12. Fénéant, S. Dimer structure of acetic acid in various solvents. Compt. rend., 235, 240 (1952).

13. Finch, J. N., and E. R. Lippincott. Hydrogen bond systems. Temperature dependence of O-H frequency shifts and O-H band intensities. J. Chem. Phys., 24, 908 (1956).

14. Hammaker, R. M. A spectroscopic investigation of the hydrogen bond: alcohols in an inert solvent. Ph. D. Thesis, Northwestern University, 1961, 150 p.

15. _____. A spectroscopic investigation of the hydrogen bond: alcohols in an inert solvent. Ph. D. Thesis, Northwestern University, 1961, p. 87.

16. Harris, J. T., Jr., and M. E. Hobbs. A study of the association of some organic acids by infrared absorption measurements. J. Am. Chem. Soc., 76, 1419 (1954).

17. Hodgman, C. D., R. C. Weast, and C. W. Wallace. Handbook of Chemistry and Physics, Chemical Rubber Publication Co., Cleveland, Ohio, 42 Ed., 1960, 2248 p.

18. Huggins, C. M., G. C. Pimentel, and J. N. Shoolery. Proton magnetic resonance studies of the hydrogen bonding of phenol, substituted phenols and acetic acid. J. Phys. Chem., 60, 1311, (1956).

19. Johnson, E. W., and L. K. Nash. The vapor phase association of acetic and trimethylacetic acids. J. Am. Chem. Soc., 72, 547 (1950).

20. Liddel, U., and E. D. Becker. Temperature-dependent absorption by CH_3OH and $CHCl_3$ in 3 region. J. Chem. Phys., 25, 173 (1956).

21. _____ and _____. Infrared spectroscopic studies of hydrogen bonding in methanol, ethanol, and t-butanol. Spectrochim. Acta., 10, 70 (1957).

22. Marshall, M., and Francis T. Fox. Microdiffusion of C_1 through C_5 organic acids. Anal. Chem., 30, 140 (1958).

23. Maryott, A. A., M. E. Hobbs, and P. M. Gross. Electric polarization of carboxylic acids. A study of the association of some additional carboxylic acids in benzene solution. J. Am. Chem. Soc., 71, 1671 (1949).

24. Pimentel, G. C., and A. L. McClellan. The Hydrogen Bond, W. H. Freeman and Co., San Francisco and London, 1960, 6 p.

25. _____ and _____. The Hydrogen Bond, W. H. Freeman and Co., San Francisco and London, 1960, p. 2.

26. _____ and _____. The Hydrogen Bond, W. H. Freeman and Co., San Francisco and London, 1960, pp. 157-165.

27. Pimentel, G. C., and A. L. McClellan. The Hydrogen Bond, W. H. Freeman and Co., San Francisco and London, 1960, p. 247.

28. _____ and _____. The Hydrogen Bond, W. H. Freeman and Co., San Francisco and London, 1960, pp. 351-352.

29. _____ and _____. The Hydrogen Bond, W. H. Freeman and Co., San Francisco and London, 1960, pp. 207, 350-386.

30. Pople, J. A., W. G. Schneider, and H. J. Bernstein. High-resolution Nuclear Magnetic Resonance, McGraw-Hill Book Co., Inc., New York, Toronto and London, 1959, 407 p.

31. Pohl, H. A., M. E. Hobbs and P. M. Gross. Electric polarization of carboxylic acids in dilute solutions of non-polar solvents. J. Chem. Phys., 9, 408 (1941).

32. Prigogine, I. The Molecular Theory of Solutions, Interscience Publishers Inc., New York, 1957, 310 p.

33. Prigogine, I., and R. DeFay. Chemical Thermodynamics, translated by D. H. Everett, Longmans Green and Co., London, 1954, 409-431 pp.

34. Reeves, L. W. Hydrogen bonding in solutions of substituted acetic acids. Can. J. Chem., 39, 1711 (1961).

35. Smith, F. A., and E. C. Creitz. Solvent effect. Steric hindrance and association of many alcohols. J. Research Natl. Bur. Standards, 46, 145 (1951).

36. Saunders, M., and J. B. Hyne. Study of hydrogen bonding in systems of hydroxylic compounds in CCl_4 through the use of NMR. J. Chem. Phys., 29, 1319 (1958).

37. Weltner, William, Jr. The vibrational spectrum, associative and thermodynamic properties of acetic acid vapor. J. Am. Chem. Soc., 77, 3941 (1955).

THE ASSOCIATION OF TRIMETHYLACETIC ACID IN CARBON TETRACHLORIDE

by

TEH-CHING CHIANG

B. S., Taiwan Normal University, Taipei, Formosa, 1960

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

The association of trimethylacetic acid in CCl_4 solution as a function of concentration over a temperature range 11° to 50°C has been studied by using infrared and proton magnetic resonance spectroscopic techniques. The concentration range studied by the IR method is 1.8×10^{-4} to 3.3×10^{-3} M, and the concentration range studied by the PMR method is 0.16 - 8M.

It was found that carefully dried materials are essential to obtain correct and reproducible data. Consequently all materials were carefully dried by known techniques and all handling of materials was carried out in a dry box.

Trimethylacetic acid has been found to undergo cyclic dimer association through hydrogen bonding formation in CCl_4 solution. The monomer $\rightleftharpoons$ cyclic dimer equilibrium constants have been evaluated by quantitative measurements of the absorption intensity of the sharp O-H stretching band (monomer band) at 3530 cm^{-1}. The results from the O-H stretching mode have been checked by measuring the absorption intensity of C = O stretching at 1750 cm^{-1} (monomer) and 1700 cm^{-1} (dimer), and results from the O-H and C = O modes show good agreement. Changes in standard enthalpy, free energy and entropy for the cyclic dimer formation of trimethylacetic acid in CCl_4 solution have been evaluated by means of the temperature variation studies. The results are in agreement with analogous measurements for similar systems.

The monomer O-H chemical shifts at 11°, 21.5°, 34° and 50°C have been evaluated by employing the equilibrium constants obtained from the IR method. The dimer O-H chemical shifts at the four temperatures have

also been measured experimentally. From the monomer and dimer O-H chemical shifts variation with temperature, it is concluded that there is a specific interaction of trimethylacetic acid with CCl_4 analogous to hydrogen bonding and might be considered as a weak type of hydrogen bonding to the solvent.